. M. SAPERS, O. PANASIUK, F. B. TALLEY and S. F. OSMAN
USDA Eastern Marketing & Nutrition Research Div.
ARS, Eastern Regional Research Lab., Philadelphia, PA 19118
and R. L. SHAW
Red River Valley Potato Processing Lab.,[1] East Grand Forks, MN 56721

FLAVOR QUALITY AND STABILITY OF POTATO FLAKES
Volatile Components Associated with Storage Changes

INTRODUCTION

DEHYDRATED POTATO products undergo two distinct types of flavor change during storage: flavor defects arising from reducing sugar-amino acid interactions and flavor defects associated with lipid oxidation. The relative extent of these changes depends on product composition, processing conditions, the presence of additives, product moisture content and storage conditions (Burr, 1966).

Potato flakes, a form of dehydrated mashed potato, have a shelf life of only 6 months in air at room temperature, even when stabilized by the incorporation of sulfur dioxide and antioxidants and by drying to an optimal moisture content (Cording et al., 1961; Strolle and Cording, 1965). Preliminary experiments conducted at the Eastern Marketing & Nutrition Research Div. (EMN) and reports from commercial producers of potato flakes (Sapers, 1970, unpublished data) have indicated that the shelf life of this product is usually limited by the development of hay-like off-flavors, attributed to oxidation, rather than to nonenzymatic browning. Potato flake instability is considered by the processing industry to be a significant problem.

Research was undertaken at EMN to establish the causes of flavor defects in potato flakes in terms of specific volatile compounds and their precursors, to relate flavor defects to specific raw material, processing, packaging and storage variables, and to develop procedures to improve product flavor and storage stability. Changes in volatile components associated with the development of off-flavors during storage are reported herein.

EXPERIMENTAL

Materials and storage conditions

Potato flakes were prepared from recently harvested (Fall, 1970) Pontiac potatoes (specific gravity 1.080–1.085) at our Red River Valley Potato Processing Laboratory (RRVPPL), East Grand Forks, Minn., using the USDA process (Cording et al., 1957). Two products were prepared: one contained no added antioxidants; the other contained Tenox 4 (20% BHA, 20% BHT, 60% corn oil), which was added to the cooked mashed potatoes, before drying, at the rate of 1.5 ml/50 lb (approximately .028%, moisture-free basis). Upon receipt at the laboratory, these products were found to contain 6.4 and 8.1% moisture, and 1000 and 1660 ppm SO_2 (moisture-free basis), respectively. Both products were packaged in No. 10 cans under air and under nitrogen (less than 2% oxygen) and were stored at 0° and 73°F.

A commercial potato flake product which had been prepared from recently harvested (Fall,1970) Kennebec potatoes by a conventional process similar to that used at RRVPPL (with added antioxidants) and shipped to us in bulk was repacked in No. 10 cans under air and under nitrogen and was also stored at 0° and 73°F. This product contained 4.7% moisture and 330 ppm SO_2 (moisture-free basis).

Sensory evaluation

Samples were removed from storage at intervals for evaluation by a 15-member trained panel which had previously been familiarized with the flavor of fresh and stored potato flakes. The samples were reconstituted without added milk, butter, or salt by mixing 60g of flakes with 1 cup of boiling water and 1/3 cup of cold water. An additional 1/2 cup of hot water was added to obtain the desired texture. Samples were served in aluminum foil dishes and examined under green light. Panelists were asked to compare the flavor of coded samples, including a hidden standard, with a standard which had been stored under nitrogen at 0°F using a five-point rating scale ranging from five, "same as standard," to one, "extreme off-flavor." The significance of differences reported by the panel was determined using Duncan's multiple range test (LeClerg, 1957).

Headspace vapor analyses

Headspace vapor analyses for lower boiling volatile components were performed on all dehydrated potato products using a modification of the procedure of Sapers et al. (1970). A ground glass joint was substituted for the rubber stopper used with the original flask-stopper assembly. Vapor samples were analyzed with a Hewlett-Packard Model 7624A Gas Chromatograph using dual 12 ft, 1/8 in. stainless steel columns containing 15% Carbowax 20M on 80/100 acid washed Chromosorb W, a helium flow rate of 15 ml/min, and flame ionization detectors. The injection port and detector temperatures were 200°C and the column temperature was programmed as follows: 60°–70°C at 1°C/min, 70°–100°C at 2°C/min, 15 min isothermal at 100°C. Retention time and peak area measurements were made using a Hewlett-Packard Model 3370A Electronic Digital Integrator.

Preparation and analysis of potato volatile concentrates

Concentrates of higher boiling potato volatiles were prepared from all dehydrated potato

Table 1—Flavor changes in potato flakes during storage

Storage conditions			Product flavor[a]					
			RRVPPL[b] flakes				Commercial flakes	
			Without antioxidants		With antioxidants			
Time (Mo.)	Temp (°F)	Atm	Score	Description	Score	Description	Score	Description
3	73	Air	4.19	Like std	4.13	Like std	3.71[c]	Hay
	73	N_2	4.19	Like std	4.44	Like std	4.32	Like std
	0	N_2	4.44	Like std	4.25	Like std	4.79	Like std
6	73	Air	3.07[d]	Hay	4.71	Like std	3.59[d]	Hay
	73	N_2	4.53	Like std	4.71	Like std	4.53	Like std
	0	N_2	4.67	Like std	4.71	Like std	4.65	Like std
9	73	Air	–	–	3.78[c]	Hay	–	–
	73	N_2	–	–	4.50	Like std	–	–
	0	N_2	–	–	4.57	Like std	–	–

[a]All samples, including a hidden standard, compared with a standard stored under nitrogen at 0°F.
[b]Red River Valley Potato Processing Lab.
[c]Significant at .05
[d]Significant at .01

products using a modification of the procedure described by Sapers et al. (1971). Ground 280-g samples of potato flakes were dispersed in 4 liters of distilled water, preheated to approximately 95°C, to form a slurry which was steam distilled at atmospheric pressure as previously described. Distillates, adjusted to pH 8 by the addition of saturated $NaHCO_3$ solution, were saturated with Na_2SO_4 and then extracted with freshly distilled diethyl ether. Ether extracts were dried over anhydrous Na_2SO_4 and concentrated to approximately 0.5g by refluxing under nitrogen, a portion of condensing solvent being continuously removed by the nitrogen stream. Potato volatile concentrates prepared by this procedure were stored at −18°C for no more than 3 days before being analyzed. 10 μl of an internal standard solution (1.76 μg ethyl butyrate/μl diethyl ether) were added to each concentrate immediately prior to its analysis.

A 2-μl aliquot of each potato volatile concentrate was analyzed using the chromatographic apparatus employed for headspace vapor analysis. The injection port and detector temperatures were 250°C, and the column temperature was programmed as follows: 4 min at 60°, 60°–80° at 1°/min, 80°–120° at 4°/min, 6 min at 120°, 120°–160° at 2°/min, 20 min at 160°C. The helium flow rate was 17 ml/min.

All samples were analyzed in duplicate. Component concentrations were expressed as mean peak area ratios, obtained by calculating the ratio of the component peak area to the area of the internal standard (ethylbutyrate) peak for the same analysis, and then averaging the ratios for replicate analyses.

The aroma of components separated by this procedure was determined by diverting half of the GC column effluent through a TC detector heated to 250°C and by smelling the gas stream at the detector exit port during the course of the analysis.

Mass spectral analyses

GC-MS analyses were carried out on headspace vapor and volatile concentrate samples using a Varian 1740 Gas Chromtograph interfaced with a jet separator to a du Pont 21-492 Mass Spectrometer. Spectra were obtained using a scan rate of 100 sec/decade, an ionization voltage of 70 ev, inlet temperatures of 150° and 200°C and source temperatures of 200° and 220°C for headspace vapor and volatile concentrates, respectively. Chromatographic columns and conditions were identical to those described previously.

All GS-MS identifications reported herein were based on analyses of experimentally produced dehydrated potato pieces rather than with potato flakes since the latter yielded insufficient volatile material. The potato pieces were processed from Maine Katahdin and North Dakota Manona tubers using the process described by Turkot et al., 1966. No antioxidants were used; both products contained approximately 1000 ppm SO_2. The dehydrated Katahdin pieces were held at 100°F under N_2 until judged by the trained taste panel to have a moderate scorched off-flavor level and were then used as a source of volatile browning products. The dehydrated Manona pieces, which were more easily oxidized and less subject to nonenzymatic browning than the Katahdin pieces, were stored in air at 73°F until judged by the panel to have a moderate oxidized off-flavor level and were then used as a source of volatile oxidation products.

Gas chromatographic comparisons of potato pieces and flakes stored under comparable conditions demonstrated that the headspace vapor and volatile concentrate chromatograms for both products were qualitatively similar. Volatile components which were increased in one product by storage in air or under nitrogen at elevated temperatures showed a similar response in the other product. The odor of such components (observed at the detector exit port) was found to be the same with both products. On the basis of these observations, the GC-MS data obtained with dehydrated potato pieces was applied to potato flakes.

RESULTS & DISCUSSION

Flavor changes during storage

The flavor scores of potato flake samples stored for 3, 6 and 9 months in air at 73°F and nitrogen at 73° and 0°F are summarized in Table 1. Flakes produced at our Red River Valley Potato Processing Lab. which contained BHA and BHT showed no flavor change during 6 months storage in air at 73°F; a slight off-flavor was noted by the panel after 9 months storage in air at 73°F.

Flakes which did not contain added antioxidants developed a moderate hay-like off-flavor during 6 months storage in air at 73°F. Samples of commercial flakes developed a slight to moderate hay-like flavor during 3 months in air at 73°F.

The hay-like off-flavor noted with air-packed flakes was similar to the flavor defect found in oxidized potato granules, characterized by Buttery (1961), and differed from the rancid off-flavor previously encountered in oxidized explosion puffed potatoes (Sapers et al., 1970).

No flavor changes were noted in nitro-

Table 2—Volatile products of sugar-amino acid reactions in the headspace vapor of potato flakes stored in nitrogen at 73° and 0°F

		Mean peak area ratio					
		2-Methylpropanal and Acetone[b] (Peak 9)			2- and 3-Methylbutanal[b] (Peak 14)		
Product	Storage Temp (°F)	0 Mo	3 Mo	6 Mo	0 Mo	3 Mo	6 Mo
Commercial	73	0.166	0.185	0.205	0.098	0.119	0.128
	0	–	.158	.151	–	.096	.070
RRVPPL[a] (without antioxidants)	73	.281	.362	.282	.203	.200	.209
	0	–	.265	.376	–	.196	.230
RRVPPL[a] (with antioxidants)	73	.364	.587	.385	.233	.500	.263
	0	–	.391	.646	–	.304	.464

[a]Red River Valley Potato Processing Lab.
[b]Identified by mass spectrometry and retention time

Table 3—Volatile products of sugar-amino acid reactions in volatile concentrates prepared from potato flakes stored in nitrogen at 73° and 0°F

		Mean peak area ratio								
		Furfural[b] (Peak 40)			Benzaldehyde[b] (Peak 45)			Phenylacetaldehyde[b] (Peak 51)		
Product	Storage Temp (°F)	0 Mo	3 Mo	6 Mo	0 Mo	3 Mo	6 Mo	0 Mo	3 Mo	6 Mo
Commercial	73	0.58	0.76	0.78	0.51	1.22	1.40	1.76	4.20	5.03
	0	–	.65	.61	–	.81	.97	–	3.35	4.11
RRVPPL[a] (without antioxidants)	73	.92	1.28	1.22	.72	1.11	1.17	5.67	7.14	7.98
	0	–	1.44	1.05	–	.79	.95	–	7.82	7.51
RRVPPL[a] (with antioxidants)	73	–	2.16	1.82	.91	1.08	1.57	5.90	12.8	11.1
	0	–	1.92	1.79	–	.79	1.11	–	12.4	13.4

[a]Red River Valley Potato Processing Lab.
[b]Identified by mass spectroscopy and retention time

gen-packed potato flakes stored at 73° and 0°F.

Effect of storage temperature on potato flake volatiles

Headspace vapor analyses performed on nitrogen packed RRVPPL and commercial potato flakes (Table 2) demonstrated that 6 months storage at 73°F resulted only in small increases in low boiling Strecker degradation aldehydes previously associated with "browning" off-flavors in explosion puffed dehydrated potatoes (Sapers et al., 1970) and potato granules (Buttery and Teranishi, 1963).

Analyses of volatile concentrates prepared from nitrogen packed flakes (Table 3) revealed small differences between samples stored at 73° and 0°F in levels of higher boiling compounds previously associated with off-flavors in puffed potatoes (Sapers et al., 1971). Alkylpyrazines were not evident on chromatograms and could not be detected by aroma in GLC effluents during the analysis of flake volatile concentrates. The absence of this class of compounds in flakes is probably a major factor accounting for the lack of off-flavors after storage in nitrogen.

Furfural levels showed little or no change during storage but were substantially higher in RRVPPL flakes, especially those containing antioxidants, than in the commercial flakes. This may be due to differences in the extent of heat damage during processing which would result in different levels of volatile browning products. Phenylacetaldehyde, a major component of potato flake volatile concentrates, showed a similar trend as did the lower boiling Strecker degradation aldehydes determined in the headspace vapor. Increases in levels of phenylacetaldehyde, which occurred principally during the first 3 months of storage at both 73° and 0°F, may have been due to the further reaction of browning intermediates formed during processing. Benzaldehyde levels increased in all nitrogen-packed products stored at 73°F and to a lesser extent at 0°F. Greater increases in this compound occurred in air-packed products during storage at 73°F (see Table 5). Differences between the air- and nitrogen-packed samples in levels of furfural and the Strecker degradation aldehydes were small and variable.

The absence of off-flavors in nitrogen-packed potato flakes stored at 73° and the minimal formation of "browning" volatiles in these samples during storage indicate that the shelf life of potato flakes is not normally limited by flavor defects resulting from reducing sugar-amino acid reactions. This conclusion does not apply, of course, to products which are abused during processing or storage, i.e., by exposure to excessively high temperatures. Such products might be unacceptable when fresh or after brief storage due to the presence of high levels of volatiles derived from the browning reaction. One must also consider the possibility that these volatiles, while not apparently objectionable at moderate levels, might modify the flavor contribution of compounds derived from lipid oxidation and other reactions in stored potato flakes.

Effect of storage in air on potato flake volatiles

Headspace vapor analyses of air-packed potato flake samples which developed a hay-like off-flavor during storage at 73°F (Table 4 and Fig. 1) revealed increases in n-hexanal and other compounds previously associated with lipid oxidation in various foods, for example, potato granules (Buttery, 1961) and soybean milk (Wilkens and Lin, 1970). Corresponding nitrogen-packed samples which lacked the off-flavor showed much smaller increases in these components, probably indicating the breakdown of hydroperoxides formed prior to storage and/or autoxidation involving residual headspace oxygen. The presence of antioxidants in RRVPPL flakes greatly reduced the extent of these changes during 6 months storage in air at 73°F, as one might predict from the flavor stability of this product; analytical results for 6 and 9 months were similar although flavor changes were noted after 9 months storage.

Analyses of volatile concentrates prepared form air-packed RRVPPL (no added antioxidants) and commercial flake samples after storage at 73°F (Table 5 and Fig. 2) showed substantial increases in a number of components indicative of lipid oxidation. These included n-hexanal, 2-pentenal (tentative), n-heptanal and 2-hexenal reported by Buttery (1961) in oxidized potato granules, and 2-heptanone, 2-pentylfuran and benzaldehyde reported by Buttery et al. (1970) in fresh potato. Unknown components 24 and 47

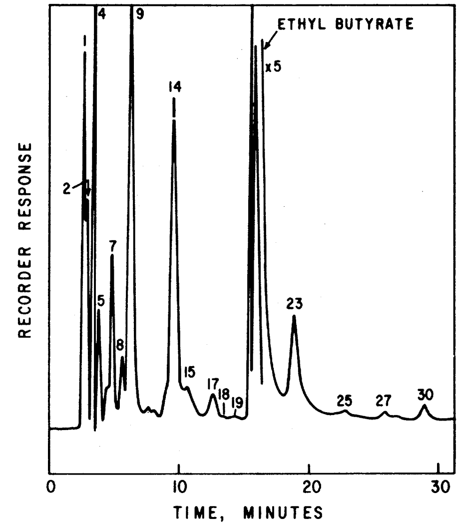

Fig. 1—Chromatogram of headspace vapor of commercial potato flakes stored 6 months in air at 73°F.

Table 4—Effect of storage in air at 73°F on the headspace vapor composition of RRVPPL[a] and commercial potato flakes

			Mean peak area ratio								
			RRVPPL[a] flakes						Commercial flakes		
			Without antioxidants			With antioxidants					
Peak No.	Identity	Method of identification[b]	0 Mo	3 Mo	6 Mo	0 Mo	3 Mo	6 Mo	0 Mo	3 Mo	6 Mo
1	Unknown	–	0.018	0.043	0.087	0.022	0.046	0.051	0.045	0.086	0.080
2	Pentane	MS, RT	.007	.048	.073	.015	.031	.027	.029	.073	.044
8	n-Propanal	MS, RT	.002	.008	.014	.002	.002	.002	.009	.018	.015
17	n-Pentanal	MS, RT	T[d]	.002	.013	T	T	.004	T	.008	.010
23	n-Hexanal	MS, RT	.012	.045	.129	.010	.016	.034	.025	.048	.084
30	2-Hexenal[c]	RT	.001	T	.005	.001	T	.001	.009	.006	.009

[a]Red River Valley Potato Processing Lab.
[b]MS = mass spectrometry; RT = retention time
[c]Tentative
[d]T = Trace

Table 5—Effect of storage in air at 73°F on the composition of volatile concentrates prepared from RRVPPL[a] and commercial potato flakes

			Mean peak area ratio								
			RRVPPL[a] flakes								
		Method of	Without antioxidants			With antioxidants			Commercial flakes		
Peak		Identifi-	0	3	6	0	3	6	0	3	6
No.	Identity	cation[b]	Mo	Mo	Mo	Mo	Mo	Mo	Mo	Mo	Mo
16	n-Hexanal	MS, RT	0.46	1.19	4.86	0.31	0.39	0.45	0.61	1.72	2.64
19	2-Pentenal[c]	MS	.06	.10	.30	.04	.05	.04	.04	.28	.38
21	n-Heptanal	MS, RT	.11	.17	.23	.12	.12	.12	.18	.35	.40
	2-Heptanone	MS, RT									
23	2-Pentylfuran	MS, RT	.01	.08	.05	T	.01	.06	.05	.21	.20
	2-Hexenal	MS, RT									
24	Unknown	–	T[d]	T	.40	T	T	.06	.02	.05	.33
45	Benzaldehyde	MS, RT	.72	1.24	2.67	.91	1.56	2.79	.51	2.33	3.65
47	Unknown	–	T	.07	.41	T	.03	.05	.20	.40	.71

[a]Red River Valley Potato Processing Lab.
[b]MS = mass spectrometry; RT = retention time
[c]Tentative
[d]T = Trace

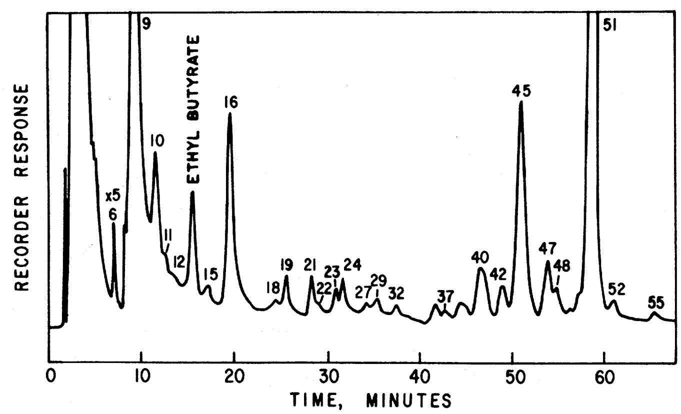

Fig. 2—Chromatogram of potato volatile concentrate prepared from commercial potato flakes stored 6 months in air at 73°F.

also increased during storage in air. Mass spectral data obtained with the latter peak [m/e 43 (100), 39 (80), 41 (60), 95 (34), 53 (28), 81 (26), 51 (20), 79 (16), 77 (14), 55 (14), 109 (4), 124 (2)] indicate that it may be a furan. Much smaller increases in the previously mentioned components (except benzaldehyde) were seen in air-packed RRVPPL flakes containing added antioxidants, even after 9 months storage at 73°F; analyses at this time were similar to those obtained at 6 months. Little or no change was seen in volatile concentrates prepared from all nitrogen-packed flake samples after storage.

GLC effluents were examined during the analysis of RRVPPL flakes (no added antioxidants) which had been stored for 6 months in air and nitrogen at 73°F to determine the odors of volatile concentrate components. While no single component had an odor identical to the hay-like off-flavor, the odors of a number of components were suggestive of oxidized off-flavors and/or were more intense in the air-packed sample than in the nitrogen-packed sample. These included aldehydic odors from peaks 10 (n-pentanal), 16 (n-hexanal), 19 (2-pentenal), 21 (n-heptanal and 2-heptanone), 23 (2-pentylfuran and 2-hexenal) and unknown component 37; a sulfury odor from peak 24; a benzaldehyde odor from peak 45 (benzaldehyde); and a green-bean odor from peak 47. The hay-like off-flavor probably represents a blend of these and perhaps other flavor notes contributed by volatile components of oxidized potato flakes.

Additional examinations of GLC effluents from analyses carried out at a column temperature of 180°C instead of the standard program revealed the presence of a violet-like odor suggestive of β-ionone in both air- and nitrogen-packed samples at a time coincident with the retention time of this compound. However, quantitative comparisons were precluded by the absence of a measurable peak at the retention time of β-ionone with these and all other oxidized flake samples. This is not surprising in view of the extremely low odor threshold of β-ionone (0.007 ppb) reported by Buttery et al. (1971). The presence of this compound would be indicative of carotenoid oxidation (Ayers et al., 1964).

The conspicuous increase in benzaldehyde in air-packed flake samples during storage is noteworthy. This compound has been identified in many food products besides potatoes and may arise from a number of sources including sugar caramelization (Hodge, 1967), phenylalanine-sugar reactions (Ramshaw and Dunstone, 1969), the oxidation or thermal degradation of compounds derived from lignin (Kazeniac and Hall, 1970) and the thermal oxidation of lipids (Kawada et al., 1967). Antioxidants apparently do not inhibit its formation.

It can be concluded from these data that the hay-like off-flavor in aged potato flakes results from oxidation and may be due at least in part to the flavor contributions of the products of lipid oxidation and other components described herein. The shelf life of this product is limited by these oxidative changes, but may vary widely, even in the presence of antioxidants. Research on the cause of such variation is in progress and will be the subject of future publications.

REFERENCES

Ayers, J.E., Fishwick, M.J., Land, D.G. and Swain, T. 1964. Off-flavor of dehydrated carrot stored in oxygen. Nature 203: 81.

Burr, H.K. 1966. Compounds contributing to flavor of potatoes and potato products. Proceedings Plant Science Symposium, p. 83. Campbell Institute for Agricultural Research.

Buttery, R.G. 1961. Autoxidation of potato granules. Part 2. Formation of carbonyls and hydrocarbons. J. Agr. Food Chem. 9: 248.

Buttery, R.G. and Teranishi, R. 1963. Measurement of fat autoxidation and browning aldehydes in food vapors by direct vapor injection gas-liquid chromatography. J. Agr. Food Chem. 11: 504.

Buttery, R.G., Seifert, R.M., Guadagni, D.G. and Ling, L.C. 1971. Characterization of additional volatile components of tomato. J. Agr. Food Chem. 19: 524.

Buttery, R.G., Seifert, R.M. and Ling, L.C. 1970. Characterization of some volatile potato components. J. Agr. Food Chem. 18: 538.

Cording, J. Jr., Eskew, R.K., Salinard, G.J. and Sullivan, J.F. 1961. Vitamin stability in fortified potato flakes. Food Technol. 15: 279.

Cording, J. Jr., Willard, M.J. Jr., Eskew, R.K. and Sullivan, J.F. 1957. Advances in the dehydration of mashed potatoes by the flake process. Food Technol. 11: 236.

Hodge, J.E. 1967. Origin of flavor in foods. Nonenzymatic browning reactions. In "Symposium on Foods: The Chemistry and Physiology of Flavors," ed. Schultz, H.W., Day, E.A., and Libbey, L.M. The Avi Publishing Co., Inc., Westport, Conn.

Kawada, T., Krishnamurthy, R.G., Mookherjee, B.D. and Chang, S.S. 1967. Chemical reactions involved in the deep fat frying of foods. 2. Identification of acidic volatile decomposition products of corn oil. J. Am. Oil Chemist's Soc. 44: 131.

Kazeniac, S.J. and Hall, R.M. 1970. Flavor chemistry of tomato volatiles. J. Food Sci. 35: 519.

Le Clerg, E.L. 1957. Mean separation by the functional analysis of variance and multiple comparisons. ARS 20-3, U.S. Dept. of Agric.

Ramshaw, E.H. and Dunstone, E.A. 1969. Volatile compounds associated with the off-flavor in stored casein. J. Dairy Res. 36: 215.

Sapers, G.M., Osman, S.F., Dooley, C.J. and Panasiuk, O. 1971. Flavor quality of explosion puffed dehydrated potato. 3. Contribution of pyrazines and other compounds to the toasted off-flavor. J.Food Sci. 36: 93.

Sapers, G.M., Sullivan, J.F. and Talley, F.B. 1970. Flavor quality in explosion puffed dehydrated potato. 1. A gas chromatographic method for the determination of aldehydes associated with flavor quality. J. Food Sci. 35: 728.

Strolle, E.O. and Cording, J. Jr. 1965. Moisture equilibria of dehydrated mashed potato flakes. Food Technol. 19: 853.

Turkot, V.A., Sullivan, J.F., Cording, J. Jr. and Eskew, R.K. 1966. Explosive puffing enhances quick-cook qualities. Food Eng. 38(12): 77.

Wilkens, W.F. and Lin, F.M. 1970. Gas chromatographic and mass spectral analyses of soybean milk volatiles. J. Agr. Food Chem. 18: 333.

Ms received 2/13/72; revised 4/2/72; accepted 4/6/72. j